

# Arylidene Polymers III. A New Route for the Synthesis of Conjugated Polymers and Copolymers of Arylidencycloalkanones, Characterization, and Some Molecular Orbital Studies of Its Model

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## SYNOPSIS

A new class of polyconjugated polymers, namely poly(2,5-arylidencyclopentanone) and poly(2,6-arylidencyclohexanone) has been obtained by condensation of cyclopentanone or cyclohexanone with terephthalaldehyde using alcoholic potassium hydroxide as a catalyst. Copolymerization of the corresponding monomers was also carried out. To characterize these polymers model compounds were prepared from cyclopentanone or cyclohexanone and benzaldehyde. The structures of the model compounds were elucidated by IR, NMR, and elemental analyses. The polymers produced were characterized by elemental analysis, IR, UV, viscometry, DSC measurements, thermogravimetric, and X-ray analyses. From the SCF-CI calculations, the 2,5-dibenzylidenecyclopentanone, as a model compound, has the *trans* form. Furthermore, the charge densities of this model, its anionic and cationic forms, as well as the ionization potential and the electron affinity have been calculated.

## INTRODUCTION

Interest in the electrical properties of conjugated organic polymers is well established, and a great variety of such materials have received attention.<sup>1-11</sup> These materials are prepared by polymerization of simple monomers that are able to form networks of highly delocalized electrons.

In this study we wish to present a route for the synthesis of some new poly- and copolyconjugated polymers containing cycloalkanone rings in the main chain. Influence of the monomer structure upon the polymer properties such as thermostability, solubility, and crystallinity were studied. Moreover, some molecular orbital calculations of 2,5-dibenzylidenecyclopentanone as a model compound have been performed using SCF-CI.

## EXPERIMENTAL

### Monomers

Cyclopentanone and cyclohexanone were purchased from Aldrich and distilled prior to use. Terephthalaldehyde was purchased from Merck and crystallized twice from water. Potassium hydroxide was analytical grade. All other chemicals were highly pure and were purified by standard methods.

### Measurements

The elemental analyses were done on a Perkin-Elmer 240 C instrument. The IR spectra were recorded on a Pye Unicam SP3 100 spectrophotometer using KBr pellet technique. <sup>1</sup>H-NMR spectra were run on a Varian EM 390-90 MHz NMR spectrometer at room temperature in CDCl<sub>3</sub> using TMS as the internal reference. The UV visible spectra were scanned on a Varian CARY 219 spectrophotometer in sulfuric acid. The inherent viscosities of polymer

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solutions (0.5 g/100 mL) in sulfuric acid were determined at 30°C using a Ubbelohde suspended level viscometer. The solubility of polymers was examined using 0.02 g of polymer in 3–5 mL of solvent at room temperature. X-ray diffractographs were obtained with Philips X-ray PW 1710 diffractometer, using Ni-filtered  $\text{CuK}\alpha$  radiation. Thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) were carried out in air with Du Pont, Model 951, 910 and Du Pont 1090 thermal analyzers at a heating rate of 10°C/min. The SCF-CI calculations were performed on a computer Model Copam, PC-401 Turbo.

### Synthesis of Model Compounds, Polymers, and Copolymers

#### Model Compounds

2,5-Dibenzylidenecyclopentanone (DBCp) and 2,6-dibenzylidenecyclohexanone (DBCh) were prepared as reported in the literature<sup>12</sup> and gave satisfactory elemental and spectral analyses.

#### Polymerization

In a three-necked flask, a mixture of 0.1341 g (1 mmol) terephthalaldehyde and 0.0841 g (1 mmol) cyclopentanone or 0.0981 g (1 mmol) cyclohexanone was dissolved in 50 mL ethanol and mechanically stirred under a stream of dry nitrogen at room temperature, 25°C. A few drops of 5% alcoholic solution

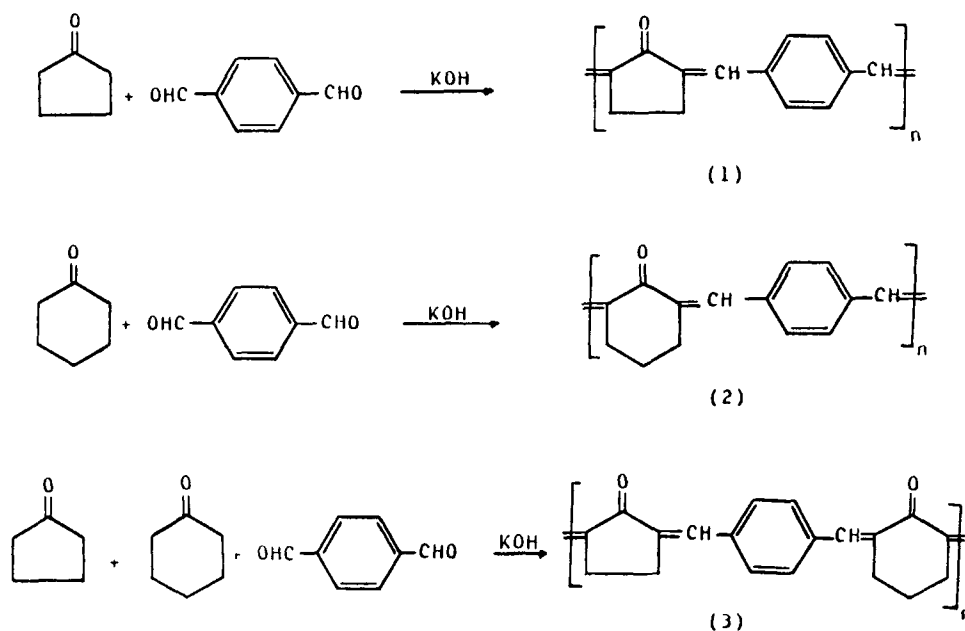
of potassium hydroxide was added, and the temperature was allowed to rise to 45°C over 15 min. At the end of this time, the polymer was precipitated. The formed polymer was filtered off, washed several times with water, ethanol, and acetone, and dried under vacuum (1 mm Hg) at 90°C for two days, yield 96%.

#### Copolymerization

A similar procedure was applied as described earlier. The copolymer was synthesized by interaction of 0.1341 g (1 mmol) terephthalaldehyde with a mixture of 0.0425 g (0.5 mmol) cyclopentanone and 0.0495 g (0.5 mmol) cyclohexanone, yield 98.3%.

## RESULTS AND DISCUSSION

The literature reveals that interaction of dialdehyde (terephthalaldehyde) and diamines leads to polyamines as typically conjugated polymers by step growth polycondensation reaction.<sup>13</sup> Knoevenagel condensation of terephthalaldehyde and *p*-bis(cyanomethyl) benzene or 2,6-bis(cyanomethyl)pyridine has also been reported<sup>14</sup> for the synthesis of macromolecular systems with conjugated double bonds. This current work presents a route for the synthesis of a new class of conjugated polymers and copolymers. Some molecular orbital calculations of its model compound are obtained and discussed.



Scheme 1

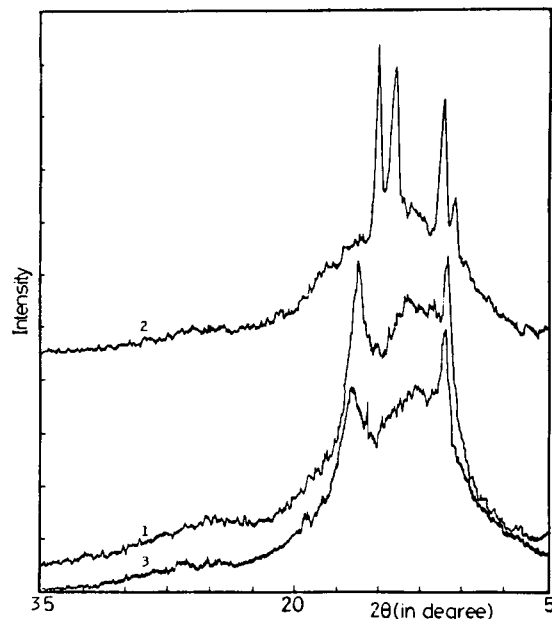
**Table I** Physical Properties of Polymers

Polymer	$a_{\eta}$ (dL/g)	Color	Yield (%)
1	0.22	Yellow	97
2	0.23	Deep yellow	96
3	0.21	Yellowish	98

<sup>a</sup> Inherent viscosity in concentrated H<sub>2</sub>SO<sub>4</sub> (0.5 g/100 mL) at 30°C.

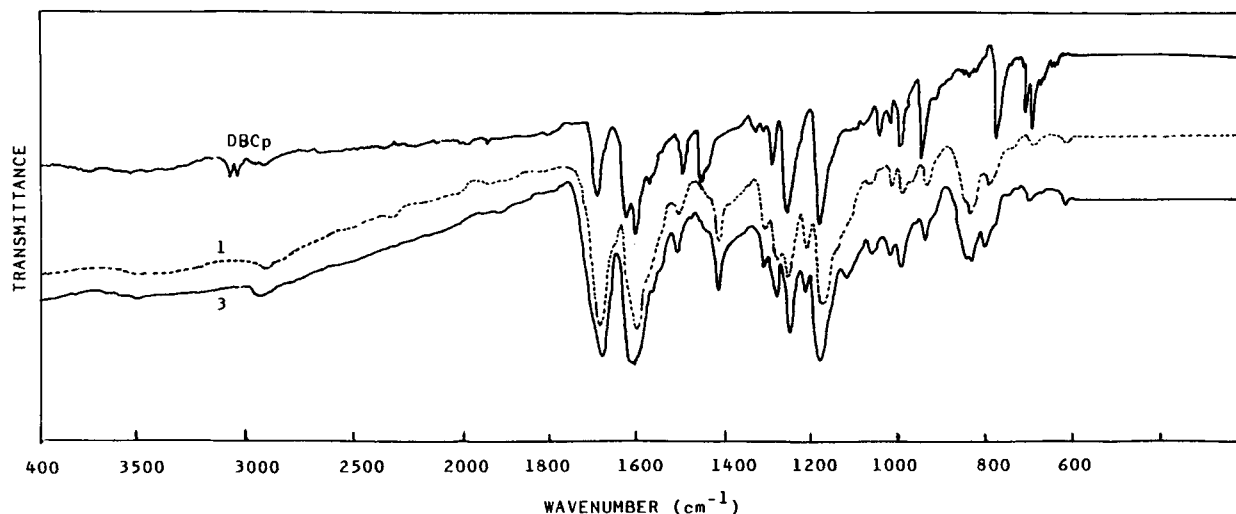
Condensation of terephthalaldehyde with cyclopentanone and/or cyclohexanone in alcoholic potassium hydroxide gave polyconjugated polymers, namely poly(2,5-benzylidenecyclopentanone) PBCp 1 and poly(2,6-benzylidenecyclohexanone) PBCh 2. Copolycondensation of equimolar quantities of terephthalaldehyde with a mixture of cyclopentanone and cyclohexanone under the same conditions gave the copolymer 3 (Scheme 1).

The polycondensation and copolycondensation were also performed with an acidic catalyst (anhydrous zinc chloride or hydrochloric acid) and at ambient temperature; however, the yields were only quantitative with a basic catalyst and at a temperature of 45°C. Early precipitation of polymers, within 15 min after mixing the monomers, indicated that the polymers were insoluble in the ethyl alcohol. This behavior might be responsible for the low degree of polymerization as shown by their inherent viscosities (Table I). These polyconjugated polymers were insoluble in almost all organic solvents such as acetone, ethyl acetate, benzene, chloroform, dichloroethane, acetonitrile, nitrobenzene, sym-

**Figure 2** X-ray diffraction patterns of polymers 1, 2, and 3.

tetrachloroethane, and partially soluble in polar aprotic solvent as dimethylformide, *N*-methyl-2-pyrrolidinone, *N,N*-dimethylacetamide and dimethylsulfoxide. In polar protic acids such as sulfuric acid, trifluoroacetic acid, and methansulfonic acid, the polymers were soluble at 30°C. All the polymers formed had yellow color, which indicates the presence of extended conjugation.

To characterize these polymers, a model compound of dibenzylidenecyclopentanone (DBCp) and dibenzylidenecyclohexanone (DBCh) was synthe-

**Figure 1** IR spectra of polymer 1, copolymer 3, and model DBCp.

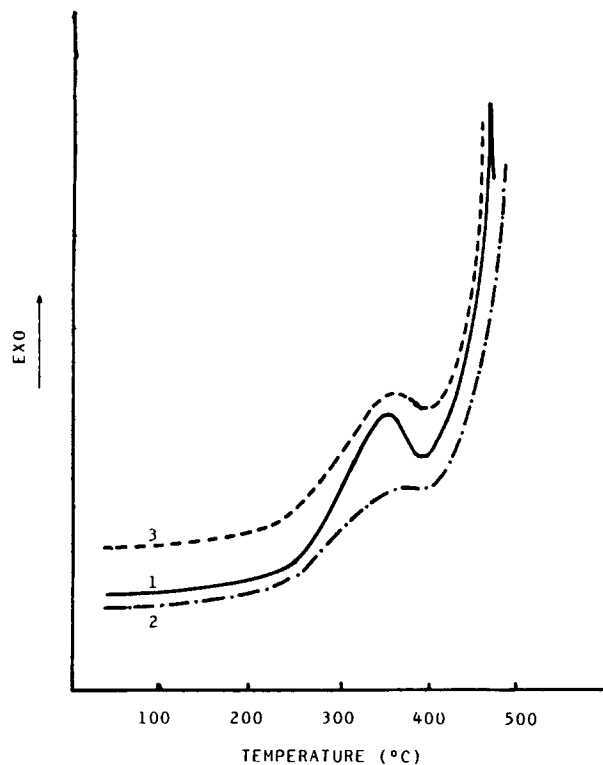


Figure 3 DSC curves of polymers 1, 2, and 3.

sized by the interaction of benzaldehyde with cyclopentanone (Cp) or cyclohexanone (Ch) in the presence of alcoholic potassium hydroxide. The struc-

tures were elucidated by elemental and spectral analyses. The IR spectrum of DBCp showed characteristic absorption bands, at  $1690\text{ cm}^{-1}$  for  $\text{C}=\text{O}$  of cyclopentanone and at  $1600\text{ cm}^{-1}$  ( $\text{C}=\text{C}$  stretching vibration). For DBCh the spectrum showed a characteristic absorption band at  $1665\text{ cm}^{-1}$  due to  $\text{C}=\text{O}$  of cyclohexanone.  $^1\text{H-NMR}$  for DBCp ( $\delta/\text{CDCl}_3/\text{TMS}_{\text{int}}$ ) gave at  $\delta 3$  (s, 4H,  $2\text{CH}_2$  of cyclopentanone), at  $\delta 7.15\text{--}7.35$  (m, 10H of Ar-H), and at  $\delta 7.55$  (m, 2H of 2CH) ppm. For DBCh ( $\delta/\text{CDCl}_3/\text{TMS}_{\text{int}}$ ) gave at  $\delta 1.65$  (m, 2H of  $\text{CH}_2$ ), at  $\delta 2.85$  (m, 4H of  $2\text{CH}_2$  of cyclohexanone), at  $\delta 7.15\text{--}7.55$  (m, 10H, of Ar-H), and at  $\delta 7.7$  (s, 2H of 2CH) ppm. All the spectra in Figure 1 show characteristic absorption bands, at  $1665\text{--}1695\text{ cm}^{-1}$  assigned to the  $\text{C}=\text{O}$  stretching, at  $2950\text{ cm}^{-1}$   $\text{C-H}$  aromatic stretching, and at  $1620$ ,  $1580$ , and  $1510\text{ cm}^{-1}$  aromatic in-plane skeletal stretching of semiunsaturated  $\text{C}=\text{C}$ . The NMR spectra of polymers and copolymers could not be recorded because of their limited solubility in the common deuterated solvents.

Ultraviolet visible spectra were obtained for the models and the polymers in sulfuric acid at concentration of  $2.6 \times 10^{-6}\text{ M}$  and displayed two absorption bands with  $\lambda_{\text{max}}$  at  $245\text{ nm}$  due to  $\pi\text{--}\pi^*$  transition within the benzenoid system, and that with  $\lambda_{\text{max}}$  at  $330\text{ nm}$  due to  $\pi\text{--}\pi^*$  excitation of  $\alpha,\beta$ -unsaturated ketone. The UV spectra of the polymers showed absorption bands broadened and small bathochromic shifting of both bands, indicating a high conjugated

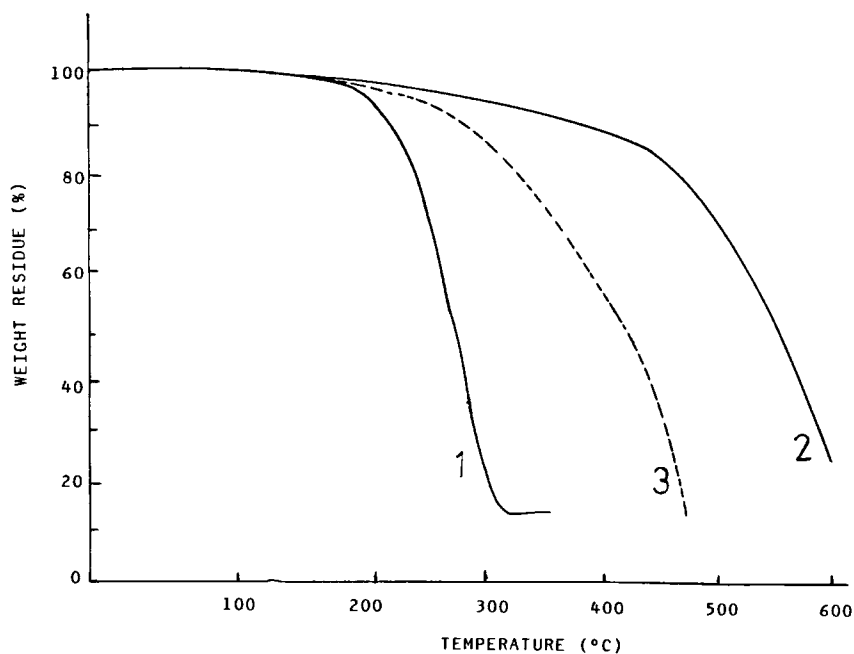


Figure 4 TGA thermograms of polymers 1, 2, and 3.

**Table II Thermal Properties of Polymers**

Polymer	Mass Loss (%)						
	200°C	225°C	250°C	275°C	300°C	350°C	400°C
1	0	11.2	12	16	35	40	50
2	0	0	0	6.7	7	8	21
3	0	0	0	8.1	9	20	28

system. It should be noted, however, that the UV visible light spectroscopy becomes insensitive to increasing conjugation above a conjugated length of about six repeat units,<sup>15</sup> and thus this method cannot be used as a quantitative technique for assaying polymers.

X-ray diffractograms of polymers 1, 2 and copolymer 3 showed a few reflection peaks intermediate between crystalline and amorphous interferences. This indicates that there is a large class of structures intermediate in ordered states between crystal, with pronounced long-range order, and anisotropic liquid with short-range order in the arrangement of its atoms and molecules (Fig. 2). Moreover, the presence of C=O as polar groups in addition to high C=C bond levels induces some order between two adjacent chains in the polymer leading to some extent of crystallinity.<sup>16</sup> Also, the diffractogram indicated that PBCh 2 has a high de-

gree of crystallinity in comparison with PBCp 1 and the copolymer 3.

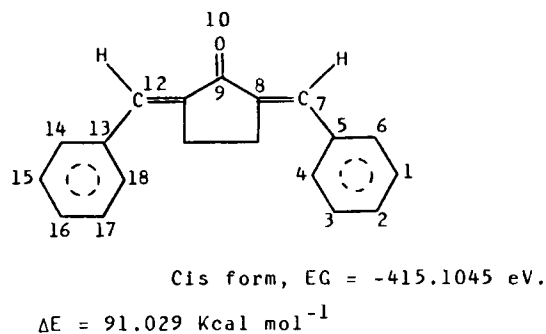
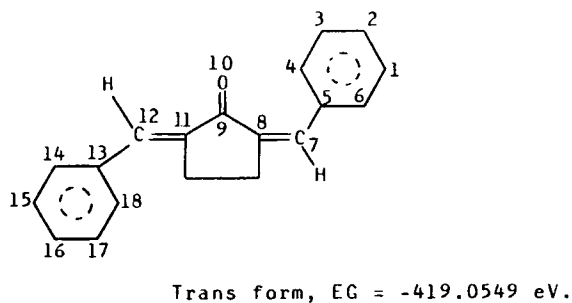
Thermal characterization of polymers was carried out by DSC and TGA in air. Figure 3 shows typical DSC traces of polymer 1, 2 and copolymer 3. The large exotherms were attributed to thermal degradation because the TGA thermograms of these polymers showed considerable rate of weight loss at the respective temperature. Figure 3 shows that a broad exotherm appeared above 200°C. Since TGA traces did not show thermal degradation at this temperature, this exotherm should be attributed to curing reactions involving the olefinic bonds.<sup>17</sup> In addition, the DSC thermograms showed different  $T_c$  and  $T_m$  for polymers 1, 2, and 3. The magnitude of the crystalline melting was proportional to the degree of crystallinity observed in the X-ray diffractographs. The TGA thermograms of the polymers are shown in Figure 4, and the weight losses corresponding to temperatures are given in Table II. The

**Table III SCF-HOMO and LUMO of 2,5-Dibenzylidenecyclopentanone as a Model Compound**

Atom	HOMO	LUMO
1	0.10148	0.04864
2	0.27243	-0.20699
3	0.10148	0.04864
4	-0.19473	0.18216
5	-0.25234	-0.13734
6	-0.19473	0.18216
7	0.24089	-0.36340
8	0.32731	0.24065
9	-0.04719	0.38766
10	-0.44586	-0.45184
11	0.32731	0.24065
12	0.24089	-0.36340
13	-0.25234	-0.13734
14	-0.19473	0.18216
15	0.10148	0.04864
16	0.27243	-0.20695
17	0.10148	0.04864
18	0.19473	0.18210

**Table IV Charge Densities of the Model Molecule and Its Cationic and Anionic Forms**

Atom	Model	Cation	Anion
1	-0.00015	+0.01015	-0.00252
2	+0.00672	+0.08094	-0.03612
3	-0.00015	+0.01015	-0.00252
4	+0.00724	+0.04515	-0.02595
5	-0.00182	+0.06185	-0.02068
6	+0.00724	+0.04515	-0.02595
7	+0.05192	+0.10995	-0.08014
8	-0.01417	+0.09295	-0.07209
9	+0.18209	+0.18431	+0.03181
10	-0.29569	-0.09690	-0.49985
11	-0.01417	+0.09295	-0.07209
12	+0.05192	+0.10995	-0.08014
13	-0.00182	+0.06185	-0.02068
14	+0.00724	+0.04515	-0.02595
15	-0.00015	+0.01047	-0.00252
16	+0.00672	+0.08094	-0.03612
17	-0.00015	+0.010147	-0.00252
18	+0.00724	+0.04515	-0.02595



Scheme 2

relative thermal stabilities of polymers could be evaluated by comparing the initiation temperature of degradation as determined by the intersection of the tangent to steepest portion of the TGA curve with its straight-line part before the polymer degradation. The TGA data showed that the thermal stabilities of the polymers were in the order of  $2 > 3 > 1$ .

The SCF-CI calculations have been done according to the literature.<sup>18</sup> From the self-iterative eigenvectors of the self-iterative eigenfunctions of the HOMO and the LUMO (Table III), the carbonyl group has a considerable contribution in the LUMO, hence it can be easily reduced. From a general point of view, the HOMO and the LUMO are mainly localized over the arylidene moiety; therefore, this moiety is sensitive toward oxidation (as a cationic form) and for reduction (as an anionic form) especially the carbonyl oxygen atom (Table IV). The ionization potential and the electron affinity have been calculated, and they have the values 8.348 and 3.858 eV, respectively.

From the  $\pi$ -electron energy of the ground state, the *trans* form is lower than the *cis* form by 91.029 Kcal/mol, hence, this model compound has the *trans* form as is shown in Scheme 2.

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